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Photopolymerizable polymer composites based on dimethacrylate systems have been increasingly utilized as dental restorative materials. One of the biggest drawbacks of current dental resin systems is the volume shrinkage and shrinkage 5 induced stresses that arise during the polymerization. Other major problems include incomplete double bond conversion and insufficient wear resistance. This invention involves the development of an entirely novel approach to the photopolymerization process that utilizes thiol-ene systems as low shrinkage and ultra-low shrinkage stress dental restorative materials. Compared with the traditional dimethacrylate 10 dental resins, these novel photopolymerizations have demonstrated a dramatically decreased volume shrinkage, extremely rapid polymerization, abilities to photopolymerize ultrathick materials and achieve much higher conversion, lack of oxygen inhibition and ultra-low shrinkage stress due to low volume shrinkage and drastically delayed gel point conversion. These polymers have thus shown 15 outstanding suitability as dental restorative materials.